

# BIOREMEDIATION OF SOLVENT SITES USING DIRECT HYDROGEN DELIVERY

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## INTRODUCTION

Direct hydrogen addition is a novel method to enhance the biodegradation of chlorinated solvents. In the biological reductive dechlorination reaction, dissolved hydrogen in groundwater acts as an *electron donor*, and halogenated compounds such as chlorinated solvents act as *electron acceptors* that are reduced in the reductive dechlorination process. Increasing the supply of electron donor to the dechlorinating bacteria will increase the rate of biodegradation.

Most researchers and technology developers have focused on adding an indirect electron donor (such as lactate, molasses, mulch, edible oil, or other carbon source) that is fermented by one type of bacteria to produce hydrogen (as a metabolic by-product) for the dechlorinators. This paper focuses on adding hydrogen directly to the subsurface via two different delivery systems: 1) low-volume pulsed bioparging (Newell et al., 2001), and 2) hydrogen-amended groundwater recirculation. Results from two different pilot tests are summarized.

## PILOT TEST 1: METHODS

In low-volume pulsed bioparging, small volumes of hydrogen gas from cylinders are sparged directly into the contaminated zone in short intervals. The hydrogen is pulsed to allow effective dissolution of the trapped gas into the aqueous phase without significant breakthrough to the surface.

This technology was tested during an eighteen-month pilot test at Cape Canaveral Air Station Florida. A 30 x 30 ft (9.1 m x 9.1 m) zone located 15 to 20 ft (4.6 to 6 m) below the water table in a sandy aquifer was used as the treatment zone for the pilot test. The test zone was in or very near a DNAPL source zone, as chlorinated ethene concentrations were very high (~300 mg/L).

## PILOT TEST 1: RESULTS

Three sparge points spaced 12 ft apart were used to deliver hydrogen into groundwater at regular intervals (weekly for most of the test). Table 1 shows the observed changes in concentration in the test zone.

**TABLE 1. Change in total chlorinated ethenes (CE) after  
18 months of low-volume pulsed biosparging.**

Location of Monitoring Well Group	Distance to Sparge Pts (ft)	Baseline CE Concentration (mg/L)	CE Concentration After 18 Months (mg/L)	Percent Change (%)
Close to Sparge Point	3 - 6	291	16	- 95%
Downgradient of Sparge	15	294	151	- 49%
Nitrogen Sparge Control	15	42	37	- 12%
Natural Attenuation Control	20	207	165	- 20%

As shown in Table 1 and Figure 1, wells in the hydrogen delivery zone showed greater reduction in chlorinated ethene concentrations compared to: 1) two wells located in a nitrogen control zone where nitrogen was pulsed into the subsurface at the same rate and frequency as the hydrogen sparge; and 2) two wells located in a natural attenuation control zone located outside the effective radius of the hydrogen sparge points. The greater reduction in chlorinated ethene concentrations in the hydrogen test monitoring wells compared to the control wells shows that reductive dechlorination resulted from the direct addition of hydrogen.

## **PILOT TEST 2: METHODS**

A hydrogen-amended groundwater recirculation system was installed in 2002 at Offutt AFB in Nebraska. The site was a jet engine test site with a 120ft by 160 ft TCE plume. cis-DCE is also found in groundwater, along with low levels of PCE and vinyl chloride.

The recirculation system consisted of 1 injection and 1 recovery well spaced 28 ft apart. Groundwater is pumped from the recovery well at ~ 0.4 gpm, amended with dissolved hydrogen to 0.5 mg/L, and then reinjected into the formation via the injection well.

## **PILOT TEST 2: RESULTS**

Over the first six months of operation the redox potential and dissolved oxygen concentration in the treatment zone groundwater were reduced significantly (-101.7 to -180.7 mv for redox; 0.7 mg/L to 0.3 mg/L for DO). Ferrous iron concentrations increased (from ~5 mg/L to 18 mg/L) and sulfate was depleted (from 180 mg/L to 90 mg/L). TCE concentrations have been reduced by 63% (0.38 mg/L to 0.14 mg/L), and the ratio of cis-DCE (the initial daughter product) to TCE (the parent compound) has increased significantly (from 0.25 to over 2.8). Some increased methane concentrations were observed, but remained below 1 mg/L during this phase of the test.

These preliminary results show that direct delivery of hydrogen can remove competing electron acceptors such as dissolved oxygen and sulfate from groundwater and lower redox potential. Both aerobes and sulfate reducers utilize hydrogen as an electron donor.

The hydrogen was shown to stimulate reductive dechlorination. Significant TCE removal was observed, with a 63% reduction in TCE concentration over six months of operation. The performance of the system appears to be improving over time. The pilot test is scheduled to be in operation for 16 months.

## REFERENCES

Newell, C.J., C.E. Aziz, P.E. Haas, J. B. Hughes, and T.A. Khan, 2001. Two Novel Methods for Enhancing Source Zone Bioremediation: Direct Hydrogen Addition and Electron Acceptor Diversion, Anaerobic Degradation of Chlorinated Solvents, pg. 19-26, , V. Magar, D. Fennell, J. Morse, B. Alleman, and A. Leason, eds., In Situ and On-Site Bioremediation: The Sixth International Symposium, Battelle Press, Columbus, Ohio,

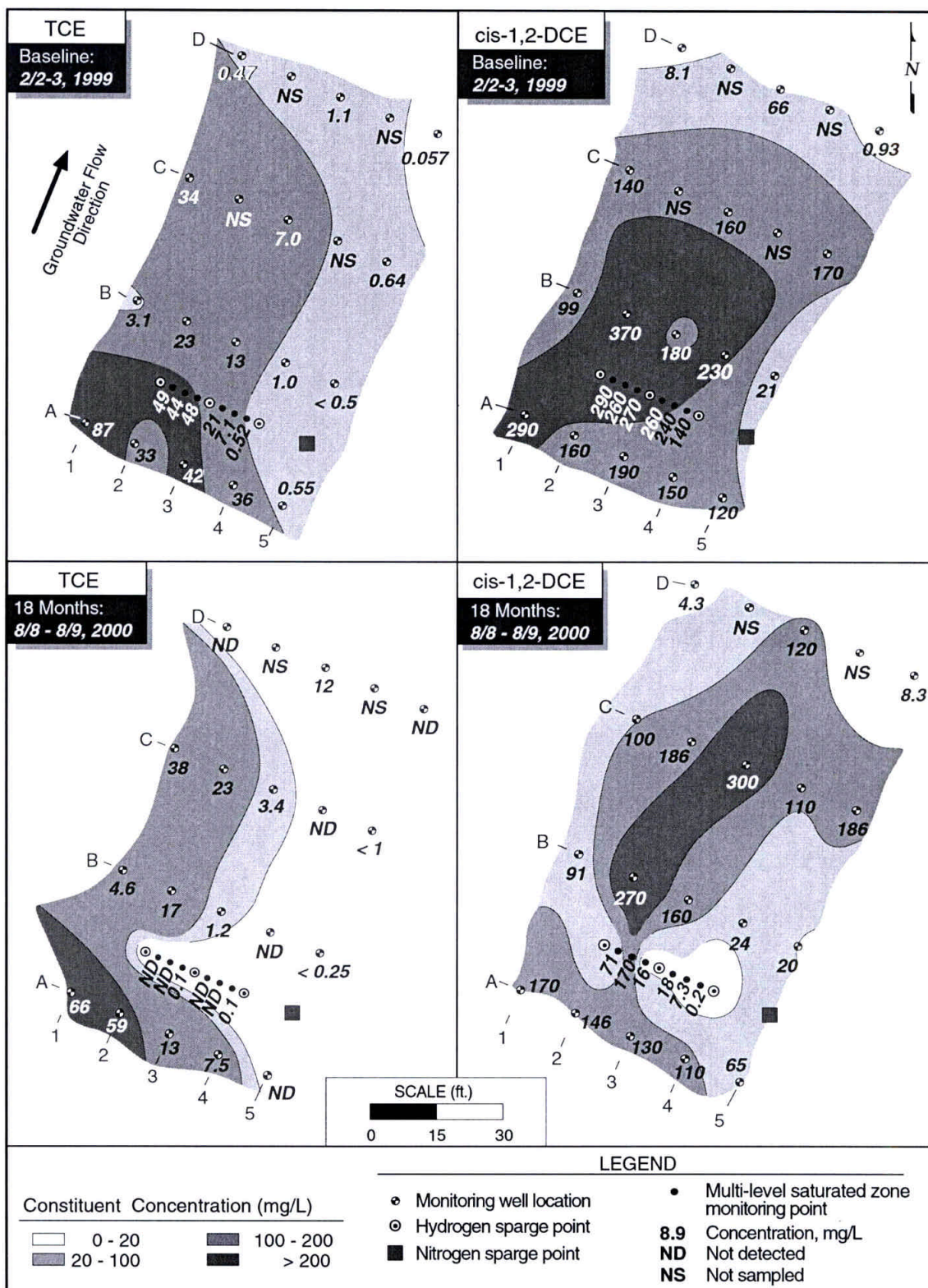


Figure 1: Change in TCE and cis-DCE Over 18 months of Low-Volume Pulsed Hydrogen Biosparging at Cape Canaveral Site